

# Spatial variability of methane emissions from Swiss alpine fens

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**Abstract** Wetland ecosystems are a major natural source of the important greenhouse gas methane ( $\text{CH}_4$ ). Among these ecosystems, fens have been shown to release high quantities of  $\text{CH}_4$ . Data on  $\text{CH}_4$  emissions from alpine fens are scarce and mainly limited to the United States and China. Therefore, static chambers were used to quantify  $\text{CH}_4$  emissions from 14 fens located in the Swiss Alps. The aims of this study were to determine the spatial variability of the emissions and to identify potential key factors which influence  $\text{CH}_4$  turnover. The fens were located at altitudes between 1,800 and 2,600 m a.s.l., the pore water varied from acidic to slightly acidic (pH 4.5–6.4) and the vegetation was dominated by plants of the genus *Carex*. In addition, the underlying bedrock was either siliceous or calcareous. Methane emissions ranged from  $74 \pm 43$  to  $711 \pm 212$  mg  $\text{CH}_4$   $\text{m}^{-2}$   $\text{day}^{-1}$ . The type of bedrock, the plant biomass above the water table and the  $\text{CH}_4$  pore water concentrations at depths from 0 to 20 cm were the main factors influencing  $\text{CH}_4$  emissions. Detailed measurements in three selected fens suggested that more than 98 % of the total  $\text{CH}_4$  emissions are due to plant-mediated transport.

**Keywords** Greenhouse gas · Wetland · Pore water profile · Dissolved organic carbon

## Introduction

Wetlands are important ecosystems with regard to the global carbon cycle and consequently exert a major impact on climatic change. Wetlands are characterized by waterlogged, anoxic conditions that result in incomplete decomposition of organic material and accumulation of carbon in the form of peat (Lai 2009). The photosynthetically active plants, mosses and algae at the surface function as a sink for atmospheric carbon dioxide. On the other hand, the deeper layers are a source for carbon dioxide and methane ( $\text{CH}_4$ ) because organic matter is decomposed under methanogenic conditions (Conrad 1996). Wetlands are the largest natural sources of atmospheric  $\text{CH}_4$ , with annual emissions of 100–230 Tg  $\text{CH}_4$ , representing 20–40 % of estimated global emissions (Denman et al. 2007). This considerable level of uncertainty arises, in part, from site-specific spatial and seasonal variability (Bubier et al. 1995a; Christensen et al. 1995; Bellisario et al. 1999; Joabsson and Christensen 2001; Whalen 2005; Sachs et al. 2010).

Wetlands are diverse and heterogeneous ecosystems characterized as bogs and fens (Whalen 2005), which are mainly distinguished by their dominant water source (Limpens et al. 2008). Bogs are ombrotrophic ecosystems with a low water input from

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precipitation, an acidic and nutrient-poor environment and dominated by bryophytes, such as *Sphagnum* species, which are slowly decomposed (Moore and Basiliko 2006; Limpens et al. 2008). Minerotrophic fens receive water and nutrients from groundwater, resulting in a more nutrient-rich environment, mainly vegetated by vascular plants that promote the gas-exchange between the subsurface and the atmosphere (Rydin and Jeglum 2006). Thus, as a consequence of the fens' minerotrophic condition, higher average water table, and vegetation type, CH<sub>4</sub> emissions from fens are generally higher than those from bogs (Whalen 2005). Methane emissions range from 10 to 180 mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> and from 30 to 400 mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> for bogs and fens, respectively (Dise et al. 1993; Bubier et al. 1995b; Bellisario et al. 1999; Chasar et al. 2000).

Most of the studies on CH<sub>4</sub> emissions in cold environments have focused on wetlands located in the northern hemisphere (Sebacher et al. 1986; Whalen and Reeburgh 1992; Bubier et al. 1995a; Christensen et al. 1995; King et al. 1998; Bellisario et al. 1999; Waddington and Roulet 2000; Whalen and Reeburgh 2000; Wagner et al. 2003; Saarnio et al. 2007; Sachs et al. 2010), as these ecosystems harbor one third of the global soil carbon (Gorham 1991; Turunen et al. 2002). Alpine wetlands have not been extensively studied and available data are mainly limited to the Rocky Mountains (West et al. 1999; Wickland et al. 2001; Chimner and Cooper 2003) and the Tibetan Plateau (Hirota et al. 2004; Cao et al. 2008; Chen et al. 2009, 2011). Very few reports have dealt with alpine wetlands in the European Alps (Koch et al. 2007; Liebner et al. 2012). Hence, detailed investigations are necessary to accurately estimate the contribution of alpine wetlands to the global CH<sub>4</sub> budget (Mast et al. 1998; Koch et al. 2007).

Methane production, oxidation, and transport from the subsurface to the atmosphere are closely linked and depend on a number of environmental factors such as temperature (Bubier et al. 1995a; Heyer et al. 2002; Koch et al. 2007), water table elevation (Freeman et al. 1992; Dise et al. 1993; Christensen et al. 1995), pH (Bubier et al. 1995b) and vegetation type (Schimel 1995; Bellisario et al. 1999; Ström et al. 2003). In order to understand and predict the CH<sub>4</sub> cycle in wetlands it is necessary to analyze the impact of each environmental factor on CH<sub>4</sub> production, oxidation and transport to the atmosphere (Bridgham et al.

2013). Methane is produced by methanogenic archaea under anoxic conditions, while methanotrophic bacteria in oxic sediment zones use the gas as a carbon and energy source (Conrad 1996).

Temperature is an important factor affecting biologically-mediated processes, and it has been reported that CH<sub>4</sub> production is more sensitive than CH<sub>4</sub> oxidation to temperature changes (Whalen 2005). In several wetland soils a close relationship between temperature and CH<sub>4</sub> emissions has been found, with emissions increasing proportionally to temperature (Bubier et al. 1995b; Heyer et al. 2002; Koch et al. 2007). Water table elevation has been identified as a good parameter to estimate CH<sub>4</sub> emissions (Bubier et al. 1995a, b; Koch et al. 2007). The water table has been suggested to affect both CH<sub>4</sub> production and CH<sub>4</sub> oxidation by regulating the position of the oxic-anoxic interface in the peat (Dunfield et al. 1993; Whalen 2005). Drought conditions have been reported to result in a lower CH<sub>4</sub> production, limited to deep anoxic soil layers, while CH<sub>4</sub> oxidation during drought was not influenced (Freeman et al. 2002). In addition, the oxic layer resulting from a decrease in the water table might support a higher decomposition of the organic material, influencing the carbon cycle in wetlands (Bardgett et al. 2008). However, the data are contradictory and the correlation between the water table elevation and CH<sub>4</sub> emissions was reported to be weak (Bellisario et al. 1999; Trudeau et al. 2013).

Peat acidity can affect CH<sub>4</sub> production and oxidation, with lower pH reducing CH<sub>4</sub> production. For example, a significant reduction in CH<sub>4</sub> production rates were reported for peat slurries incubated at a pH of 5.5 compared to incubations at pH of 7.0 (Valentine et al. 1994). However, partial adaptation of methanogenic archaea and methanotrophic bacteria to sub-optimal pH has been observed (Dunfield et al. 1993).

CH<sub>4</sub> emissions from wetlands are strongly dependent on vegetation type, as plants influence CH<sub>4</sub> production, oxidation, and transport from the subsurface to the atmosphere (Christensen et al. 2003; Ström et al. 2003). A positive correlation between plant productivity, plant biomass and CH<sub>4</sub> emission has been reported in different wetlands (Whiting and Chanton 1993; Bellisario et al. 1999; Joabsson and Christensen 2001; von Fischer et al. 2010; Chen et al. 2011).

Many vascular plants in fens have developed air channels in stems, leaves and roots (i.e. aerenchyma) to transport oxygen to submerged organs in anoxic soil

(Armstrong et al. 1991; Joabsson et al. 1999). As a consequence, the aerenchyma may also act as conduits for  $\text{CH}_4$  transport to the atmosphere, bypassing the oxic layer where biological  $\text{CH}_4$  oxidation is taking place (Bellisario et al. 1999; Whalen 2005). Several studies addressing atmospheric  $\text{CH}_4$  emission therefore focused on wetlands dominated by *Carex* spp. (Whiting and Chanton 1992; Chasar et al. 2000; Ding et al. 2004). It has been reported that more than 90 % of the  $\text{CH}_4$  emitted in *Carex* spp. dominated wetlands passes through their aerenchyma system (Whiting and Chanton 1992). In contrast, in a laboratory study using peat cores dominated by *Sphagnum* spp. and cores dominated by *Juncus* spp. lower  $\text{CH}_4$  emissions were observed from the cores vegetated by vascular plants (Roura-Carol and Freeman 1999). Vascular plants also stimulate  $\text{CH}_4$  production through secretion of root exudates and provision of plant litter to the methanogenic archaea (Whiting and Chanton 1992). In addition, vascular plants transport oxygen to the rhizosphere which stimulates the activity of methanotrophic microorganisms (Bellisario et al. 1999).

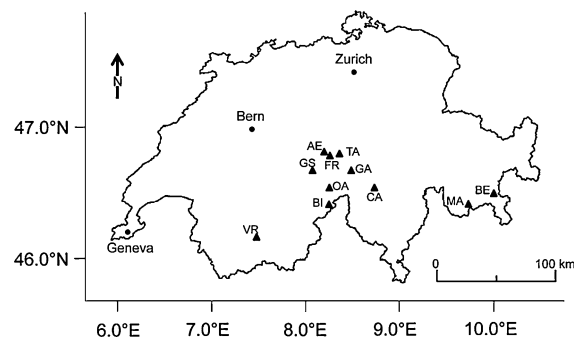
A field survey was conducted to quantify  $\text{CH}_4$  emissions from fens located in the Swiss Alps. The Swiss Alps are characterized by two main bedrock types (siliceous and calcareous) which are the dominant influence on the soil properties (Lazzaro et al. 2009). Calcareous bedrock is composed of large amounts of  $\text{CaCO}_3$  that result in a more alkaline soil and a lower availability of nutrients compared to siliceous bedrock.

The specific goals of this study are (i) to assess the spatial variability of  $\text{CH}_4$  emissions from alpine fens located on siliceous or calcareous bedrock in Switzerland, (ii) to quantify  $\text{CH}_4$  pore water concentrations of these fens, and (iii) to conduct a statistical analysis in order to relate  $\text{CH}_4$  emissions to selected environmental factors (e.g. bedrock and vegetation type, plant biomass, soil and air temperature, and dissolved organic carbon [DOC] concentrations).

## Materials and methods

### Sampling sites

Fourteen different alpine fens in the Swiss Alps were selected (Fig. 1). The main criteria for choosing these fens were (i) a water table above the soil surface and



**Fig. 1** Location of the selected fens in the Swiss Alps: Aelggi (AE), Bernina (BE), Binntal (BI), Cadagno (CA), Frutt (FR), Göschener Alp (GA), Grosse Scheidegg (GS), Maloja (MA), Oberaar (OA), Tannalp (TA) and Val de Réchy (VR)

(ii) a vegetation cover mainly composed of plants of the genus *Carex*. The 14 alpine fens in this study varied in altitude, bedrock type, yearly mean precipitation, as well as type of plant cover (Table 1). The sites are generally characterized as snow-covered in winter and with a 3–4 month long snow-free summer. The average annual precipitation data at each site was obtained from the CLIMAP database of the Swiss Federal Office of Meteorology and Climatology (<http://meteoswiss.ch>; Table 1). Altitudes ranged from 1,800 to 2,600 m a.s.l.; six fens were located on calcareous bedrock and eight fens on siliceous bedrock. Most fens on siliceous bedrock were dominated by *Carex nigra*, while *C. rostrata* was the main vegetation on the calcareous bedrock (Table 1). Fens with an area ranging from 10 to 800 m<sup>2</sup> were chosen, with the exception of the Oberaar fen one, which covers an area of 3,000 m<sup>2</sup>. There was one study site per fen and these study sites were characterized as nutrient-poor to mesotrophic (Rydin and Jeglum 2006). Most of the study sites were sampled once, in either 2010 or 2011, between July and August (Table 2). However, two sites (GA and OA1) were sampled twice, once in 2010 and once in 2011. The microbiological structures of the fens at Oberaar and Göschener Alp have been described by Franchini and Zeyer (2012) and by Liebner et al. (2012), respectively.

### Quantification of methane emissions

Methane emissions into the atmosphere were measured between noon and 3.00 p.m. using static transparent chambers (30 × 30 × 30 cm, volume of

**Table 1** Characterization of fens selected for this study

Fen	Site	Coordinates	Altitude (m a.s.l.)	Bedrock	Mean precipitation (mm)	Vegetation <sup>a</sup>														
						CR	CN	CS	CL	EA	ES	TC	EF	SP	JU	CA				
Aelggi	AE	8°13'55.4"E 46°47'12.5"N	1,820	Calcareous	800	X														
Bernina	BE	10°1'33.8"E 46°25'5.5"N	2,410	Siliceous	630		X							X						
Binntal	BI	8°15'52.0"E 46°22'36.4"N	2,000	Calcareous	1,000	X														X
Cadagno	CA	8°42'54.0"E 46°32'38.5"N	2,020	Calcareous	1,400		X								X					
Fruitt	FR	8°15'31.2"E 46°46'20.3"N	1,910	Calcareous	800	X														X
Göschener Alp	GA	8°29'39.9"E 46°38'58.2"N	1,920	Siliceous	1,700	X			X											X
Grosse Scheidegg	GS	8°6'14.9"E 46°39'29.1"N	1,930	Calcareous	1,300	X														X
Maloja	MA	9°42'25.7"E 46°22'29.9"N	1,930	Siliceous	630		X								X					
Oberaar fen 1	OA1	8°15'40.4"E 46°32'50.3"N	2,320	Siliceous	1,700	X	X	X					X	X	X					X
Oberaar fen 2	OA2	8°15'39.5"E 46°32'49.8"N	2,320	Siliceous	1,700	X	X	X					X	X	X					X
Tannalp	TA	8°19'46.3"E 46°46'53.1"N	2,010	Calcareous	800	X														X
Val de Réchy fen 1	VR1	7°30'23.8"E 46°11'25.9"N	2,340	Siliceous	650		X								X					X
Val de Réchy fen 2	VR2	7°30'30.2"E 46°9'34.2"N	2,310	Siliceous	650		X								X					X
Val de Réchy fen 3	VR3	7°30'5.6"E 46°10'37.6"N	2,570	Siliceous	650		X								X					X

<sup>a</sup> Vegetation: CR, *Carex rostrata*, CN, *C. nigra*, CS, *C. sempervivens*, CL, *C. limosa*, EA, *Eriophorum angustifolium*, ES, *E. scheuchzeri*, TC, *Trichophorum caespitosum*, EF, *Equisetum fluviatile*, SP, *Sphagnum* sp., JU, *Juncus* sp., CA: *Calliergon* sp.

**Table 2** Physico-chemical characteristics of each site at the time of sampling

Site	Date	Water table <sup>d</sup> (cm)	Air temperature (°C)	Soil temperature (°C)		pH	Conductivity ( $\mu\text{S cm}^{-1}$ )		DOC ( $\text{mg C L}^{-1}$ )	
				0–20 cm <sup>e</sup>	20–50 cm <sup>e</sup>		0–50 cm <sup>e</sup>	0–20 cm <sup>e</sup>	20–50 cm <sup>e</sup>	
AE <sup>a</sup>	08/24/11	3.0	22.2	17.9 ± 2.0	14.0 ± 0.8	6.4 ± 0.3	395.4 ± 160.0	15.4 ± 15.9	41.1 ± 25.3	
BE <sup>b</sup>	08/03/10	4.0	13.9	14.6 ± 2.4	11.4 ± 0.4	5.4 ± 0.2	147.5 ± 16.6	4.7 ± 1.4	5.9 ± 1.6	
BI <sup>b</sup>	08/09/10	5.0	22.0	14.3 ± 2.0	13.0 ± 0.6	6.0 ± 0.2	694.2 ± 144.6	7.1 ± 4.4	4.5 ± 2.1	
CA <sup>c</sup>	07/22/10	4.0	17.0	15.5 ± 0.6	n.d.	4.7 ± 0.1	94.6 ± 10.1	12.3 ± 8.2	n.d.	
FR <sup>a</sup>	08/06/11	5.0	21.6	18.8 ± 1.7	n.d.	4.5 ± 0.2	16.1 ± 4.1	12.2 ± 1.6	n.d.	
GA <sup>b</sup>	07/08/10	2.0	24.2	20.7 ± 4.8	13.8 ± 2.4	4.8 ± 0.2	73.2 ± 18.3	10.2 ± 4.0	9.3 ± 2.5	
GA <sup>a</sup>	08/25/11	6.0	20.0	19.3 ± 1.5	15.2 ± 1.9	4.6 ± 0.1	14.5 ± 1.7	10.1 ± 2.1	9.8 ± 1.6	
GS <sup>a</sup>	08/11/11	6.0	18.3	18.5 ± 2.6	13.2 ± 0.6	5.0 ± 0.3	25.8 ± 5.1	8.2 ± 9.5	9.1 ± 12.0	
MA <sup>b</sup>	08/04/10	4.0	15.5	15.1 ± 2.2	15.0 ± 1.0	5.5 ± 0.2	211.4 ± 60.2	13.3 ± 15.6	19.5 ± 19.7	
OA1 <sup>c</sup>	07/24/10	4.0	5.8	9.2 <sup>f</sup>	9.7 ± 0.9	5.2 ± 0.2	92.1 ± 10.4	2.0 ± 1.4	9.5 <sup>f</sup>	
OA2 <sup>c</sup>	07/24/10	4.0	5.8	9.2 <sup>f</sup>	9.1 <sup>f</sup>	6.0 ± 1.3	99.0 ± 28.2	2.8 ± 0.9	18.3 <sup>f</sup>	
OA1 <sup>a</sup>	08/05/11	5.0	15.8	15.9 ± 1.5	12.7 ± 1.0	5.0 ± 0.3	19.4 ± 5.4	8.1 ± 4.4	10.1 ± 9.3	
TA <sup>a</sup>	08/23/11	4.0	27.0	20.0 ± 1.9	14.9 ± 1.5	6.2 ± 0.1	254.8 ± 47.3	4.1 ± 1.9	2.9 ± 1.6	
VR1 <sup>b</sup>	08/10/10	3.0	18.0	14.9 ± 1.4	n.d.	6.3 ± 0.2	826.3 ± 123.1	7.4 ± 8.6	n.d.	
VR2 <sup>b</sup>	08/11/10	3.0	13.4	14.4 ± 0.3	n.d.	5.1 ± 0.4	90.0 ± 18.0	11.5 ± 1.8	n.d.	
VR3 <sup>b</sup>	08/11/10	1.0	13.8	16.3 ± 1.8	n.d.	6.3 ± 0.1	603.8 ± 125.1	2.7 ± 0.5	n.d.	

n.d. not determined, pore water could not be extracted

<sup>a</sup> Four profiles

<sup>b</sup> Two profiles

<sup>c</sup> One profile

<sup>d</sup> Water table elevation above the soil surface

<sup>e</sup> Below the water table, the average values within these depths are presented

<sup>f</sup>  $n < 3$  values

0.027 m<sup>3</sup>), as described in Liebner et al. (2012). At each site, four chambers were gently placed into standing water within a radius of 5 m. Sampling was performed using portable walkways to minimize disturbance. For each chamber, the average height between the water table elevation and the top of the chamber was measured and the volume of the headspace was recorded. After several minutes of equilibration, the openings on the top of the chamber were carefully closed with butyl rubber stoppers. A needle connected to a 50 mL syringe was inserted through a stopper. The chambers were not equipped with fans and therefore the piston of the syringe was pulled and pushed five times to mix the gas in the chamber. Immediately after mixing, a 50 mL gas sample was taken and injected into a 20 mL glass vial, which had been previously flushed with N<sub>2</sub> and evacuated. This procedure was repeated every 5 min up to 30 min (seven samples in total).

Concentrations of CH<sub>4</sub> were measured by gas chromatography (Trace GC Ultra; Thermo Electron Corporation, Rodano, Italy) using a 2 m Porapak N 100/120 mesh column (1/16" outer diameter and 1 mm inner diameter) and a flame ionization detector (FID). The column and detector temperatures were set at 30 and 250 °C, respectively. The carrier gas (N<sub>2</sub>) flow velocity was 30 mL min<sup>-1</sup> (30 kPa); the FID hydrogen was set at 35 kPa and the synthetic air flow at 350 kPa. Peak areas calibration was performed with Messer CAN-Gas standards (CH<sub>4</sub> in synthetic air 5.0, Messer Schweiz AG, Lenzburg, Switzerland) over a concentration range from 1 to 5,000 ppm and integrated using the software Chromeleon (Vers. 6.8, Dionex AG, Olten, Switzerland).

The emission of CH<sub>4</sub> into the atmosphere was calculated from the CH<sub>4</sub> accumulated in the chamber over 30 min using linear regression (van der Nat and Middelburg 1998; Ding et al. 2005; Liebner et al. 2012). Linear regression with  $r^2 < 0.95$  was omitted from further analyses. The increase in CH<sub>4</sub> concentrations was linear and no ebullition was observed in our measurements.

#### Plant species and biomass

After each emission measurement the plant biomass covered by the chamber was harvested by clipping the plants at the water table with scissors. The plant material was wrapped in aluminum foil and taken to

the laboratory. Dead biomass (i.e. brown and black residues of stems and leaves) was discarded and the remaining live biomass (i.e. green stems and leaves) was dried at 70 °C for 48 h and weighed. Throughout this report the term "plant biomass" refers exclusively to the dry weight (units: g m<sup>-2</sup>) of live plant biomass above the water table. The plant species reported in Table 2 made up more than 95 % of the live biomass for each emission measurement.

#### Pore water sampling and physico-chemical characteristics

Pore water was sampled to obtain a profile of DOC and CH<sub>4</sub> pore water concentrations to a depth of 50 cm. The pore water was extracted along the profile using brass tubes. These tubes (0.3 cm inner diameter) were closed at one end and perforated with 0.1 cm diameter closely spaced holes for the first 1 cm from the closed end. The perforations allow the extraction of pore water and avoid the co-extraction of peat material. Nevertheless, at some sites sampling was not possible below certain depths as the peat material caused severe clogging of the brass tubes.

A series of brass tubes were inserted vertically into the water/soil to allow extraction of the pore water profile at the following depths below the water table: 1.0 (considered to reflect the surface water conditions), 2.5, 5.0, 7.5, 10.0, 15.0, 20.0, 30.0, 40.0 and 50.0 cm. Each tube was connected to a three-way valve (Discofix C-3, Braun Melsungen AG, Melsungen, Germany) by silicon tubing. Seven mL of pore water (equivalent to the dead volume of the tube) was pulled through the tube with a 10 mL syringe. The valve was subsequently closed to hold the pore water inside and to exclude oxygen contaminations from the atmosphere. After 1 h of equilibration, 7 mL of pore water was extracted and discarded.

For DOC measurements, 20 mL of pore water was collected from each depth and immediately filtered on-site through 0.45 µm nylon filters (Wicom Perfect Flow, Meienfeld, Switzerland). Before sampling, the filters were washed with 10 mL of distilled water to remove contaminants. Each filtered sample was acidified with 0.1 mL of a 1 M HCl solution (King et al. 1998) and later stored in a glass vial at -20 °C. DOC analysis was performed with a Shimadzu TOC-5000 analyzer (Shimadzu SSI, Columbia, MD).

To determine the concentration of dissolved CH<sub>4</sub> in pore water along the profile, 5 mL of pore water was collected with a 10 mL plastic syringe as described above and immediately injected into to previously N<sub>2</sub>-flushed vials containing 0.1 mL of a 1 M HCl solution (Frenzel and Karofeld 2000; Joabsson and Christensen 2001). The vials were stored at 4 °C until analysis. Methane concentrations in the vial headspace were measured by gas chromatography, and concentrations of dissolved CH<sub>4</sub> were subsequently calculated using the headspace method according to Liebner et al. (2012). At each site in 2010, one or two independent profiles of CH<sub>4</sub> pore water concentrations were measured. However, for the sites sampled in 2011, four independent profiles were measured.

Similarly, depth profiles of conductivity and pH were analyzed in situ according to Liebner et al. (2012) using a Multi 350i probe (WTW, Laboratory and Field Products, Nova Analytics, Woburn, MA) connected to a LR 325/01 conductivity cell and a SenTix 51 pH electrode. Prior to using the LR 325/01 conductivity cell, its response was tested using KCl solutions. This test demonstrated that up to 1,200 μS cm<sup>-1</sup> the signal is a linear function of the KCl concentration.

#### Oxygen and temperature measurements along the profile

Oxygen pore water concentrations along the profiles were measured in situ with a Fibox 3-trace v3 planar trace oxygen minisensor (PreSens, Regensburg, Germany), as previously reported (Liebner et al. 2012). Temperature and oxygen pore water concentrations were logged after an equilibration time of about 15 min at the same depths as for DOC and CH<sub>4</sub>. However, at some sites oxygen pore water concentrations were determined colorimetrically using a DRr890 colorimeter (HACH Lange, Rheineck, Switzerland) with high and low range AccuVac Dissolved Oxygen Reagent Ampules (HACH Lange). 25 mL of pore water was extracted from the brass tubes as previously described. Approximately 5 mL was slowly discarded to avoid exposure of the water samples to air, and 20 mL was transferred immediately to the AccuVac glass ampules and measured using the DRr890 colorimeter (HACH Lange).

The colorimetric method was used at sites BI, MA, VR1, VR2 and VR3, whereas the oxygen minisensor

method was used at all other sites. Both methods have been applied in environmental studies (e.g. Kleikemper et al. 2005; Liebner et al. 2012); however, each method also has limitations: The minisensor method is temperature dependent and requires long equilibration times. Moreover, in peat soil the measuring device can clog. On the other hand, the colorimetric method requires large volumes of pore water, and the samples can be exposed to air prior to measurement. Preliminary tests comparing the two methods showed deviations in the range of 2–25 % from each other. This is in agreement with data reported by Bagshaw et al. (2011), who also compared different methods.

#### Statistical analysis

The statistical analysis was performed with the software R (version 2.15.2) (R Development Core Team 2012). Methane emissions, plant biomass, CH<sub>4</sub>, oxygen and DOC pore water concentrations, as well as data for conductivity were logarithmically transformed to approximate normal distributions. Normality of the data was tested using the Shapiro–Wilk test. Differences between bedrock or vegetation type, and CH<sub>4</sub> emissions, plant biomass and physico-chemical parameters (e.g. soil and air temperature, DOC pore water concentrations) were identified with two-sample *t*-tests.

Linear mixed models were used to perform stepwise multiple linear regression analyses. First, the relationship between CH<sub>4</sub> emissions (dependent variable) and the following fixed parameters were evaluated: altitude, bedrock and vegetation type, plant biomass, air temperature and pressure, precipitation, and the mean values (depth 0–20 cm) of conductivity, pH, soil temperature, and CH<sub>4</sub>, oxygen and DOC pore water concentration. Second, the relationships between CH<sub>4</sub> pore water concentration (0–20 cm, dependent variable) and the following fixed parameters were evaluated: altitude, bedrock and vegetation type, plant biomass, air temperature and pressure, precipitation, conductivity, pH, soil temperature, and oxygen and DOC pore water concentration. These linear mixed models were implemented using R package “lme4” (function “lmer”) (Bates et al. 2011). The sites were included as a random effect to account for the variability observed between sites. Normality and homogeneity were examined by visually inspecting plots of the residuals against fitted

values. Selection of the best-fitting models was performed based upon Akaike Information Criterion (AIC) values, and calculated with the Restricted Maximum Likelihood (REML) (Johnson and Omland 2004). Thus, the simplest method that performed the best was applied. In addition, to assess the validity of the mixed parameter analyses, ANOVA analyses were performed comparing the models with fixed parameters to the null models with only the random effect. Results in which the model including fixed effects did not differ significantly from the null models were rejected. The significance level for all tests was  $P = 0.05$ . Pore water below 20 cm was not included in this analysis because of difficulty sampling below this depth.

## Results

### Physico-chemical characteristics of the fen pore water

Physico-chemical characteristics are summarized in Table 2. At all sites the water table elevation varied from 1 to 6 cm above the soil surface. From 0 to 20 cm, soil temperatures differed substantially between the study sites ( $9.2$  to  $20.7 \pm 4.8$  °C, Table 2). These temperatures partially reflected the air temperatures at the time of sampling. In deeper soil layers the temperatures of the different sites were more equal ( $9.1$  to  $15.2 \pm 1.9$  °C).

The pH values of pore water ranged from slightly acidic (max. pH  $6.4 \pm 0.3$ ) to acidic (min. pH  $4.5 \pm 0.2$ ), and conductivities ranged broadly from  $14.5 \pm 1.7$  to  $826.3 \pm 123.1$   $\mu\text{S cm}^{-1}$ . DOC pore water concentrations varied from  $2.0 \pm 1.4$  to  $15.4 \pm 15.9$   $\text{mg C L}^{-1}$  for the first 20 cm and from  $2.9 \pm 1.6$  to  $41.1 \pm 25.3$   $\text{mg C L}^{-1}$  in deeper soil layers. No significant difference in water table elevation between sites located on siliceous and those on calcareous bedrocks was detected ( $P = 0.314$ ). Parameters, such as pH ( $P = 0.982$ ), conductivity ( $P = 0.872$ ), DOC pore water concentrations from 0 to 20 cm ( $P = 0.477$ ) and 20 to 50 cm ( $P = 0.763$ ), and soil temperatures from 0 to 20 cm ( $P = 0.148$ ) and 20 to 50 cm ( $P = 0.853$ ) did not vary significantly. Mean altitudes were  $2,257 \pm 243$  m a.s.l. and  $1,948 \pm 77$  m a.s.l. for fen sites located on siliceous and calcareous bedrock, respectively.

### Plant species and plant biomass

*C. nigra* and *C. rostrata* dominated the vegetation at the study sites. Sites on siliceous bedrock were dominated by *C. nigra*, while calcareous sites were dominated by *C. rostrata* (Table 1). This difference was not significant ( $P = 0.094$ ). The average plant biomass for *C. nigra* ranged from  $44.4 \pm 33.5$  to  $101.7 \pm 15.8$   $\text{g m}^{-2}$  and for *C. rostrata* from  $67.0 \pm 17.8$  to  $430.1 \pm 361.0$   $\text{g m}^{-2}$  (Table 3). *C. rostrata* biomass was significantly higher than *C. nigra* biomass ( $P = 0.001$ ). Moreover, plant biomass on siliceous bedrock was lower than on calcareous bedrock ( $P = 0.002$ ).

### Methane emissions

Methane emissions ranged from  $74 \pm 43$   $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  at VR3 to  $711 \pm 212$   $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  at BI during the 2010 campaign, and from  $153 \pm 31$   $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  at GA to  $539 \pm 58$   $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  at TA during 2011 (Table 2). At the sites that were sampled twice, GA and OA1,  $\text{CH}_4$  emissions in 2011 were roughly 25 % lower than emissions in 2010 (Table 2), however, the emissions were not significantly different ( $P = 0.122$ ;  $P = 0.217$ , respectively). An average  $\text{CH}_4$  emission of  $162 \pm 76$  ( $74 \pm 43$  to  $246 \pm 45$ )  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  was observed at siliceous sites, while the average emission at calcareous sites was  $503 \pm 176$  ( $328 \pm 120$  to  $711 \pm 212$ )  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ . In addition, an average  $\text{CH}_4$  emission of  $232 \pm 190$  ( $74 \pm 43$  to  $544 \pm 147$ )  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  was measured at sites covered by *C. nigra*, whereas the average emission at *C. rostrata* sites was  $398 \pm 218$  ( $153 \pm 31$  to  $711 \pm 212$ )  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ . Significant differences were found between bedrock types and  $\text{CH}_4$  emissions ( $P < 0.001$ ) and between vegetation types and  $\text{CH}_4$  emissions ( $P = 0.005$ ).

### Methane and oxygen pore water concentrations

Methane pore water concentrations were determined along a profile from the water table down to 50 cm, where extraction to this depth was possible. At all sites (except CA and OA2), in the first few cm below the water table,  $\text{CH}_4$  pore water concentrations were low but they steadily increased down to 20 cm ( $27 \pm 34$ – $273 \pm 236$   $\mu\text{M}$ ). From 20 to 50 cm,  $\text{CH}_4$  pore



**Table 3** Methane emissions and plant biomass at the different study sites

Site	Date	Vegetation <sup>a</sup>	Methane emissions (mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	Plant biomass (g m <sup>-2</sup> )
AE	08/24/11	CR	462 ± 178	430.1 ± 361.0
BE	08/03/10	CN, EA	219 ± 54	70.9 ± 8.9
BI	08/09/10	CR	711 ± 212	244.8 ± 131.0
CA	07/22/10	CN	544 ± 147	58.1 ± 9.3
FR	08/06/11	CR	328 ± 120	141.7 ± 32.8
GA	07/08/10	CR	206 ± 48	n.d.
GA	08/25/11	CR	153 ± 31	67.0 ± 17.8
GS	08/11/11	CR	421 ± 95	153.6 ± 71.2
MA	08/04/10	CN	213 ± 76	65.0 ± 14.1
OA1	07/24/10	CR	225 ± 19	n.d.
OA2	07/24/10	EA	246 ± 45	n.d.
OA1	08/05/11	CR	172 ± 69	78.8 ± 23.5
TA	08/23/11	CR	539 ± 58	205.8 ± 17.4
VR1	08/10/10	CN, SP	104 ± 55	44.4 ± 33.5
VR2	08/11/10	CN	144 ± 76	101.7 ± 15.8
VR3	08/11/10	CN	74 ± 43	70.6 ± 27.8

Mean values ( $n = 4$ ) with standard deviations are presented

*n.d.* plant biomass not determined

<sup>a</sup> See Table 1 footnotes

water concentrations remained high ( $64 \pm 71$ – $627 \pm 555 \mu\text{M}$ ) (Table 4). High CH<sub>4</sub> pore water concentrations ( $>250 \mu\text{M}$ ) were detected near the surface of the water table at CA and OA2, but at these sites pore water could not be extracted below 25 cm due to clogging. Furthermore, at CA, gas bubbles (50 % of the total volume extracted) were present in pore water samples extracted from 15 to 20 cm, resulting in high CH<sub>4</sub> pore water concentrations (Table 4). At several sites, pore water could not be extracted below 15–25 cm (12 profiles) or 30–40 cm (five profiles) (Table 4, footnotes). No significant differences were found between CH<sub>4</sub> pore water concentrations from 0 to 20 cm and bedrock types ( $P = 0.294$ ) or vegetation types ( $P = 0.143$ ). Similarly, CH<sub>4</sub> pore water concentrations at a depths 20–50 cm were not significantly different between bedrock types ( $P = 0.993$ ) or vegetation types ( $P = 0.347$ ).

Oxygen pore water concentrations generally decreased to zero within the first 20 cm below the water table (Table 4). At most sites, average oxygen pore water concentrations from 0 to 20 cm were above  $5.0 \pm 4.8 \mu\text{M}$ . Oxygen pore water concentrations were significantly different between vegetation types ( $P = 0.026$ ). Higher oxygen pore water concentrations were observed with *C. rostrata* ( $75.9 \pm 51.4 \mu\text{M}$ ) than *C. nigra* ( $24.3 \pm 19.0 \mu\text{M}$ ). From 20 to 50 cm average

oxygen pore water concentrations were lower than  $6.6 \pm 9.6 \mu\text{M}$  (Table 4) at most sites.

#### Methane and oxygen pore water concentration profiles

Some of the concentrations presented in Table 4 are based on one or two profiles or pore water samples could not be extracted below 15 or 30 cm (Table 4, footnotes) and thus this data is not presented in Fig. 2. However, at four sites sampled in 2011 (GA, GS, OA1 and TA), four independent profiles to a depth of 50 cm were measured. For these four profiles the mean values of CH<sub>4</sub> and oxygen pore water concentrations at each depth are shown in Fig. 2. At GA in 2011, CH<sub>4</sub> pore water concentrations were generally low ( $<100 \mu\text{M}$ ) and CH<sub>4</sub> pore water concentrations increased with depth (Fig. 2a). The profiles obtained at GS and TA in 2011 were quite similar to each other. The profiles were characterized by an exponential increase of CH<sub>4</sub> pore water concentrations from 0 to 7.5 cm, followed by an almost linear increase from 7.5 to 15 or 20 cm, where the highest CH<sub>4</sub> pore water concentrations were observed (Fig. 2a). Below 15–20 cm CH<sub>4</sub> pore water concentrations decreased again (Fig. 2a).

At GA in 2011, high oxygen pore water concentrations could be detected down to 30 cm (Fig. 2b). At

**Table 4** Mean CH<sub>4</sub> and oxygen pore water concentrations at two different depth intervals (0–20 cm and 20–50 cm)

Site	Date	Methane (μM)		Oxygen (μM)	
		0–20 cm <sup>d</sup>	20–50 cm <sup>d</sup>	0–20 cm <sup>d</sup>	20–50 cm <sup>d</sup>
AE <sup>a</sup>	08/24/11	92 ± 63	153 ± 37 <sup>g</sup>	83.2 ± 64.0	0.0 ± 0.0 <sup>g</sup>
BE <sup>b</sup>	08/03/10	273 ± 236	627 ± 555	31.6 ± 64.5	0.7 ± 1.2
BI <sup>b</sup>	08/09/10	244 ± 111	323 ± 47	5.2 ± 5.7	1.2 ± 1.7
CA <sup>c</sup>	07/22/10	955 ± 1124 <sup>c, f</sup>	n.d.	5.0 ± 4.8 <sup>e</sup>	n.a.
FR <sup>a</sup>	08/06/11	56 ± 90 <sup>e</sup>	n.d.	102.6 ± 91.6 <sup>e</sup>	n.a.
GA <sup>b</sup>	07/08/10	192 ± 132	178 ± 71 <sup>g</sup>	0.0 ± 0.0	0.0 ± 0.0 <sup>g</sup>
GA <sup>a</sup>	08/25/11	28 ± 53	64 ± 71	165.0 ± 58.3	39.4 ± 56.4
GS <sup>a</sup>	08/11/11	116 ± 153	255 ± 79	74.0 ± 61.6	0.0 ± 0.0
MA <sup>b</sup>	08/04/10	191 ± 145	154 ± 86	58.0 ± 87.7	0.8 ± 1.5
OA1 <sup>c</sup>	07/24/10	202 ± 93	174 ± 21 <sup>g</sup>	n.a.	n.a.
OA2 <sup>c</sup>	07/24/10	273 ± 57 <sup>e</sup>	n.d.	n.a.	n.a.
OA1 <sup>a</sup>	08/05/11	67 ± 70	130 ± 31	71.9 ± 111.4	6.6 ± 9.6
TA <sup>a</sup>	08/23/11	114 ± 120	249 ± 36	29.4 ± 33.4	0.0 ± 0.0
VR1 <sup>b</sup>	08/10/10	34 ± 68 <sup>e</sup>	n.d.	19.1 ± 22.6 <sup>e</sup>	n.a.
VR2 <sup>b</sup>	08/11/10	27 ± 34 <sup>e</sup>	n.d.	9.5 ± 15.4 <sup>e</sup>	n.a.
VR3 <sup>b</sup>	08/11/10	43 ± 51 <sup>e</sup>	n.d.	22.4 ± 42.5 <sup>e</sup>	n.a.

Mean values with standard deviations are presented

*n.d.* not determined, pore water could not be extracted, *n.a.* not analyzed

<sup>a</sup> Four profiles

<sup>b</sup> Two profiles

<sup>c</sup> One profile

<sup>d</sup> Below the water table

<sup>e</sup> Pore water extraction was not possible below 15–25 cm

<sup>f</sup> Gas bubbles were co-extracted with pore water

<sup>g</sup> Pore water extraction was not possible below 30–40 cm

GS, OA1 and TA oxygen pore water concentration profiles displayed a similar trend with concentrations close to zero from 7.5 to 15 cm (Fig. 2b).

#### Factors related to methane dynamics

Statistical analyses revealed that the CH<sub>4</sub> emissions were positively related to plant biomass and average CH<sub>4</sub> pore water concentrations from 0 to 20 cm (Table 5; Equation 1). Moreover, CH<sub>4</sub> emissions were lower on siliceous bedrock than on calcareous bedrock. Other environmental factors, such as altitude, vegetation type, pH and oxygen pore water concentration had no direct influence on CH<sub>4</sub> emissions at the studied sites.

In addition, CH<sub>4</sub> pore water concentrations from 0 to 20 cm were negatively related to oxygen pore water concentrations (Table 5; Equation 2), while other

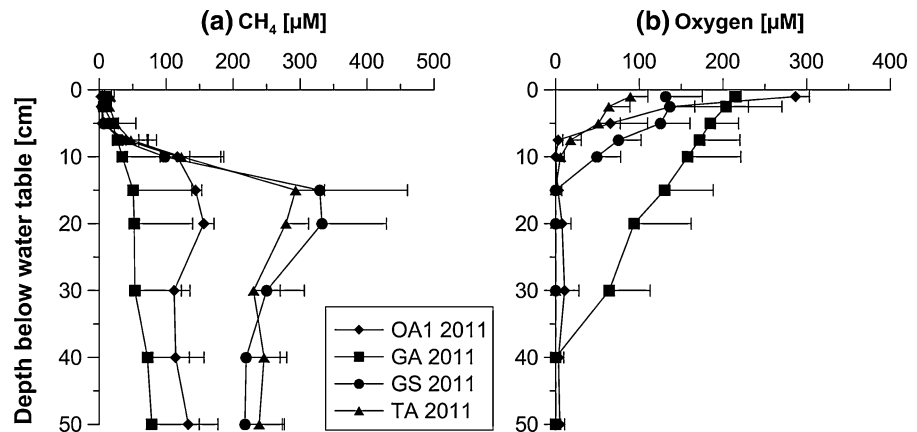
environmental factors had no direct influence on CH<sub>4</sub> pore water concentrations at shallow depths.

#### Discussion

##### Plant-mediated transport of methane from alpine fens

An almost linear increase of CH<sub>4</sub> pore water concentrations from 7.5 to 15 cm at GS and TA, and from 5 to 10 cm at OA1 was observed in 2011 (Fig. 2); therefore, the upward CH<sub>4</sub> flux in pore water using Fick's first law of diffusion was calculated similarly to Beer and Blodau (2007) and Hornibrook et al. (2009). The diffusion coefficient of CH<sub>4</sub> in water ( $D_{w, \text{methane}}$ ) was determined from the mean temperature measured in situ across the depth interval of the linear regression

**Fig. 2** Methane (a) and oxygen (b) pore water concentration profiles from four fens located in the Swiss Alps. Bars denote standard deviations of the means ( $n = 4$ )



**Table 5** Linear mixed models for  $\text{CH}_4$  emissions ( $n = 37$ ) and for  $\text{CH}_4$  pore water concentrations (depths 0–20 cm,  $n = 160$ )

Equation	Dependent variable	Linear mixed model	AIC	$P$ value
1	Methane emissions	$\log[\text{emi}] = 1.849 + 0.265 \cdot \log[\text{pla}] + 0.110 \cdot \log[\text{met}20] - 0.347 \cdot \text{bed}$	-12.5	<0.001
2	Methane pore water concentrations 0–20 cm	$\log[\text{met}] = 2.386 - 0.629 \cdot \log[\text{oxy}]$	293.4	<0.001

*Emi*  $\text{CH}_4$  emissions, *Pla* plant biomass, *Met20*  $\text{CH}_4$  pore water concentration (mean value 0–20 cm), *Bed* bedrock (calcareous = 0, siliceous = 1), *Met*  $\text{CH}_4$  pore water concentration 0–20 cm, *Oxy* oxygen pore water concentration 0–20 cm

using the polynomial regression for  $D_w$ , methane in water (83rd Edition of the Handbook of Physics and Chemistry). The diffusion coefficient of  $\text{CH}_4$  in soil ( $D_s$ , methane) was calculated using the equation (Lerman 1979):

$$D_s = D_w \varphi^2$$

where  $\varphi$  stands for porosity which was assumed to be 0.9 at shallow soil depths according to Letts et al. (2000). The calculated diffusive  $\text{CH}_4$  fluxes were 4 (OA1), 7 (GS) and 6  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  (TA), which accounts only for 2.3, 1.7 and 1.1 %, respectively, of the total  $\text{CH}_4$  emissions into the atmosphere. These emissions are in the same range of previously reported values from a Swiss alpine fen (Liebner et al. 2012). The results suggest that the  $\text{CH}_4$  transport through the aerenchyma of *C. rostrata* is the major emission pathway in the alpine fens analyzed. Similar results have been reported from other wetlands by measuring  $\text{CH}_4$  emissions in the presence and absence of plants (Whiting and Chanton 1992; Waddington et al. 1996; King et al. 1998).

Within the first 5–7.5 cm below the water table at GS and TA and 2.5–5 cm at OA1, the  $\text{CH}_4$  pore water

concentration curves have a concave shape (Fig. 2a). However, at GS and OA1 for this depth interval there was free water above the soil surface, where the governing transport mechanisms for  $\text{CH}_4$  remain unknown. Therefore, these sections of the  $\text{CH}_4$  pore water concentration profiles were not considered for further analyses. The concavity of the profiles at TA from 5 to 7.5 cm, suggested that the shallow layers are a sink for  $\text{CH}_4$ . The  $\text{CH}_4$  sink or consumption was determined by calculating the difference between upward fluxes at depths from 5 to 7.5 cm and from 7.5 to 15 cm (Fechner and Hemond 1992). A sink of 4  $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  accounts for about 67 % of the diffusive flux calculated from 7.5 to 15 cm depth, and might be the result of  $\text{CH}_4$  consumption by methanotrophic bacteria. However, we are aware that  $\text{CH}_4$  pore water concentration profiles may be subjected to spatial and temporal variability. While several studies have determined emissions to the atmosphere, these calculations aim to quantify the subsurface processes. The obtained results complement previous findings by Fechner and Hemond (1992) and Hornibrook et al. (2009).

In addition to diffusion and plant mediated transport, ebullition, has been reported to be an important

process in fens (Whalen 2005). However, ebullition was not detected during CH<sub>4</sub> flux measurements at our field sites, which is in agreement with a recent study quantifying the episodic ebullition to approximately 3 % of the total CH<sub>4</sub> emission (Green and Baird 2013).

#### Environmental factors related to methane dynamics

Methane emissions ( $74 \pm 43$  to  $711 \pm 212$  mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>) reported in this study showed high variability within and between the sites. High variability in CH<sub>4</sub> emissions has been reported in most studies where static chamber techniques have been used to quantify gas-exchanges from the subsurface to the atmosphere. Bubier et al. (1993) reported a within-site variability of CH<sub>4</sub> emissions ranging from 86 to 200 % that could be explained mainly by differences in the site microtopography. Methane emissions in our study are in the same range as those in the arctic tundra (Bartlett et al. 1992; Whalen and Reeburgh 1992).

A relationship between CH<sub>4</sub> emissions and bedrock type was found in the present study (Table 5, Equation 1). On siliceous bedrock, CH<sub>4</sub> emissions ranged from  $74 \pm 43$  to  $246 \pm 45$  mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>. These emissions are in agreement with data reported by Koch et al. (2007) and Liebner et al. (2012), who also investigated fens on siliceous bedrock. On calcareous bedrock, CH<sub>4</sub> emissions ranged from  $328 \pm 120$  to  $711 \pm 212$  mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>; however, these sites were also located at lower altitudes and plant biomass was higher. Moreover, no significant differences in physico-chemical parameters were found between sites located on siliceous and calcareous bedrock. This supports Chapman et al. (2003) who suggested that the water chemistry of fens is controlled by biologically-mediated processes rather than by water sources.

A positive correlation was found between CH<sub>4</sub> emissions and vascular plant biomass (Table 5, Equation 1), which is consistent with results reported from fens located in the northern hemisphere (Bellisario et al. 1999; Joabsson and Christensen 2001; von Fischer et al. 2010) and in alpine regions (Koch et al. 2007; Chen et al. 2011). Moreover, in most cases *C. rostrata* had higher plant biomass than *C. nigra*, which is in full agreement with data published by Visser et al. (2000). This may have an indirect influence on the CH<sub>4</sub> emissions.

A positive correlation was found between CH<sub>4</sub> emissions and CH<sub>4</sub> pore water concentrations at shallow depths (Table 5, Equation 1). In addition, CH<sub>4</sub> pore water concentrations were negatively related to oxygen pore water concentrations at the same depth (Table 5, Equation 2). Further, the aerenchyma of vascular plants allows for the diffusion of oxygen from the atmosphere down to the rhizosphere, where it stimulates the activity of methanotrophic bacteria and at the same time hampers the activity of methanogenic archaea (Whalen 2005). Furthermore, Epp and Chanton (1993) suggested that 10–90 % of CH<sub>4</sub> produced is oxidized by methanotrophic bacteria in the rhizosphere of vascular plants. Thus, the negative relationship found between CH<sub>4</sub> and oxygen pore water concentrations might result from both CH<sub>4</sub> oxidation and plant-mediated transport. Similarly, King et al. (1998) reported an inverse correlation between CH<sub>4</sub> pore water concentration and root density, where low CH<sub>4</sub> pore water concentrations were measured at depths of 15–20 cm in zones of high root densities.

#### Conclusion

The objective of this study was to quantify the CH<sub>4</sub> emissions from fens located in the Swiss Alps at 1,800–2,600 m a.s.l. The emissions ranged from 74 to 711 mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> and thus were in the same range as emissions from wetlands in northern latitudes (Alaska, Siberia, and northern Canada). Despite the fact that CH<sub>4</sub> emissions showed high spatial variability within and between the different sites the emissions could be related to environmental factors, such as bedrock type, plant biomass and CH<sub>4</sub> pore water concentration at shallow depths. However, since these environmental factors may be interdependent further study would be required to determine if they have a direct or an indirect effect. This study also demonstrates the importance of aerenchymous plants like *Carex* spp. These plants not only provide carbon substrates for the methanogenic archaea and oxygen for the methanotrophic bacteria in the subsurface but also act as major conduits for the transport of CH<sub>4</sub> from the subsurface into the atmosphere.

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